Indian J. Phys. **51A**, 282–287 (1977)

Grüneisen parameter of noble metals

L. P. Pathak and M. P. Hemkar

Physics Department, University of Allahabad, Allahabad

(*Received* 26 *July* 1976)

The temperature variation of the Grüneisen parameter for noble metals are calculated by using the modified non-central force model of Behari and Tripathi which takes Clark *et al* type angular forces and Sharma and Joshi type volume forces from the observed elastic anharmonicity. The calculation is carried out by a modified Houston's procedure. The calculated values of Grüneisen parameters are compared with the experimental observations and the results are discussed.

1. Introduction

The anharmonic effects in lattice vibrations play an important role in many solid state phenomena such as thermal expansion, temperature dependence of elastic constants, high temperature lattice specific heat, thermal conductivity etc (Ziman 1960). Of these properties, the thermal expansion is the most familiar one. Grüneisen (1926) first tried to explain the effect of anharmonicity in terms of single dimensionless parameter γ in an approximate way.

$$\gamma = \beta V/\psi C_v \qquad \ldots (1)$$

Here β is volume thermal expansion coefficient, ψ the compressibility, C_v, the specific heat at constant volume and V the crystal volume. This parameter depends on lattice vibrational frequencies. According to theory of Grüneisen, γ is assumed to be a constant, independent of lattice frequency and temperature, with a numerical value ~ 2.

Recently experimental and theoretical workers have investigated that this parameter depends on temperature and frequency of the crystal. Rubin *et al* (1961) White (1963) and Carr *et al* (1964) showed that γ varies with temperature on the basis of their experiments on the thermal expansion. The theoretical investigations of Barron (1955, 1957) and Blackman (1957, 1958, 1959) on thermal expansion by using some idealized models fr the lattice dynamics have shown that drastic variation in the value of γ with temperature may occur in the temperature region $T = 0.2\Theta$ and γ_p for some lattice mode may have negative value. Horton (1961)has calculated this parameter as a function of temperature for copper by incorporating the observed value of the temperature variation of the elastic constants into a central nearest and next nearest force-model. The agreement between theory and experiment is quite satisfactory. Sheards (1958) relates the volume dependence of the individual normal frequencies with the pressure dependence of the elastic constants for an isotropic elastic continuum.

His results for noble metals show a good agreement with the experimental data. Recently Collins (1963) have computed the temperature variation of γ for a number of materials of the cubic structure with the aid of anisotropic continuum model. Toya (1961) has studied the Grüneisen parameter from the first principles, by extending Hartree-Fock method for alkali and noble metals and found that it is function of temperature.

In this present paper we have used Behari and Tripathi's model (1969) to compute the temperature dependence of the Grüneisen parameter of noble metals copper, silver and gold from the experimentally measured values of the elastic constants and calculated pressure dependence of k_e. It was found that this model offers a fairly good explanation of lattice dynamical behaviour of many cubic metals (Prakash & Homkar 1973, 1974, Prakash *et al* 1974, 1975; Pathak *et al* 1975, 1976). It was thought worth while to compute the Grüneisen parameter on the basis of this model and to compare it with the available experimental data.

2. Theory

We know that

$$\frac{\beta V}{k_B \psi} = \sum_{q,j} \gamma_{q,j} E(x) \text{ with } x = \hbar\omega/k_B T \qquad \ldots (2)$$

where ω is the angular frequency of normal mode of wave vector q, and polarization j, k_B represents Boltzmann constant and $E(x)$ is the Einstein specific heat function

$$E(x) = \frac{x^2 e^x}{(e^x - 1)^2} \qquad \ldots (3)$$

and

$$\gamma_{q,j} = -(\partial \ln \omega_{q,j}/\partial \ln V)_T \qquad \ldots (4)$$

equation (2) gives as

$$\gamma = \frac{\sum_{q,j} \gamma_{q,j} E(x)}{\sum_{q,j} E(x)} \qquad \ldots (5)$$

Replacing the sums over allowed values of q within the first Brillouin zone by integrations in the usual manner, (5) becomes

$$\gamma = \frac{\sum_{j} d\Omega \int_0^{q_m} dq \gamma_{j(q)} E(x) q^2}{\sum_{j} d\Omega \int_0^{q_m} dq E(x) q^2} \qquad \ldots (6)$$

where Ω is the solid angle in the wave-vector space.

3. Numerical Computation

The calculation of γ at different temperature from Eq. (6) carried out by means of modified Houston's method. In an evaluation of γ the integration over q was performed numerically and integration over solid angle Ω was carried out by using the modified Houston's six-term integration procedure as developed by Betts *et al* (1956). The six directions for q used are [100], [110] [111], [210], [211] and [221] The individual phonon Gruneisen parameter $\gamma_{q,j}$ were determined in terms of elastic constants, then observed pressure derivatives. k_r as obtained by Gellman Bruckner method and its theoretically determined pressure derivatives

Table 1

Metal	Pressue derivatives of Pressure derivatives of elastic constants			Reference, Temperature variation of elastic constants		Mass a.m.u
	$\partial C_{11}/\partial p$	$\partial C_{12}/\partial p$	$\partial C_{44}/\partial p$			
Copper	5 940	5 190	2.630	a)	Overton and Gaffney[c]	63.54
Silver	5 117	3.607	3.04	a)	Neighbours and Alers[d]	107.87
	7.032	5.754	2.310	b)		
Gold	5.717	4.957	1 520	a)	Neighbours and Alers[d]	196.97
	7.014	6.138	1.790	b)		

Notes to Table 1 :

a) Hiki, Y. and Granato, A V., 1966, *Phys. Rev.* 144, 411.

b) Daniels, W B. and Smith, C. S , 1958, *Phys. Rev.* 111, 713

c) Overton, W. C. and Gaffney, J 1955, *Phys. Rev.*, 98, 969.

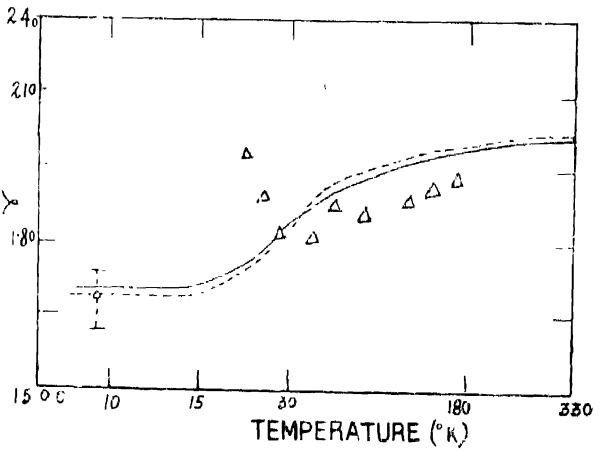
d) Neighbours, J. R. and Alers, G. A., 1958, *Phys. Rev* , 111, 707.

In computational work we have used the observed temperature variation of the elastic constants and lattice parameters. The sources of the temperature variation of elastic constants and their pressure derivatives are summarized in table 1 The lattice parameter values at various temperatures were taken from the work of Pearson (1958). For the pressure derivatives of elastic constants, we have used only experimental values at room temperature because no experimental data for them over a wide range of temperatures are available Two sets of pressure derivatives of elastic constants at room temperature (300K) have been measured by Daniels and Smith (DS) and Hiki and Granato (HG) by ultrasonic pulse method. For the metal copper two sets of measurements are almost the same, but differ much in the case of silver and gold. Here we have used in our calculations both the sets for silver and gold,

3. Results and Discussion

The calculated values of γ are plotted against temperatures in figures 1-3 for copper, silver and gold respectively. For comparison we have also depicted the experimental measurements of Rubin *et al* (1961) for copper and of Corruccini and Gniewek (1961) for silver and gold. We have also used the recent experimental data for γ of Fraser and Hollis-Hallet (1965) for these metals

A survey of Figs 1-3 reveals that there is satisfactory agreement between calculated values based on this modified model and measured values of γ for copper but not for silver and gold. It is evident from the diagrams 2 and 3 that calculated γ- T curves do not coincide for (DS) and (HG) data for pressure derivatives of elastic constants. Further it is interesting to note that the calculations using pressure derivatives data of Daniels and Smith (1958) show better agreement with experiments than the data of Hiki and Granato for silver and gold



1 The Grüneisen parameter of copper as a function of temperature. The continuous curve corresponds to present calculation. Experimental observations are indicated by —O— (Rubin *et al* 1954) Δ (Fraser and Hollis Hallet).

The discrepancies in these cases are not surprising and can be attributed to the neglect of temperature variation of pressure derivatives of elastic constants, the approximate description of the electron lattice interaction and to the assumption of the electron lattice interaction and to the assumption of short-range interaction and errors in the high temperature region by the extrapolation method. It emerges from the present study that this model provides a reasonable description of Grüneisen parameter. It is felt, therefore that use of this model in calculation of a physical property of a crystal will be more realistic. It is pertinent

to point out again that more complicated models would burden such a calculation too much.

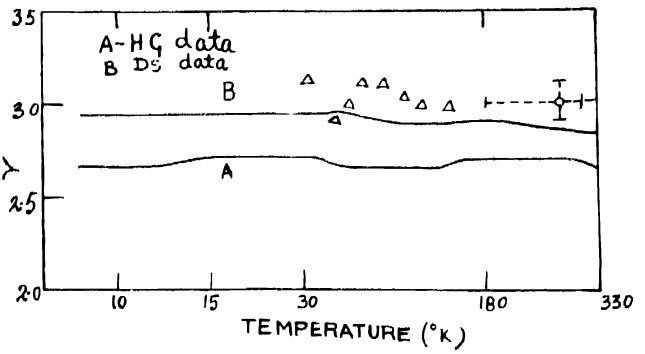


Fig. 2. The Grüneisen parameter of silver as a function of temperature. The continuous curves correspond to present calculation Experimental observations are indicated by Δ Fraser and Hallis-Hallet, —O— (Corruccini and Gniewek)

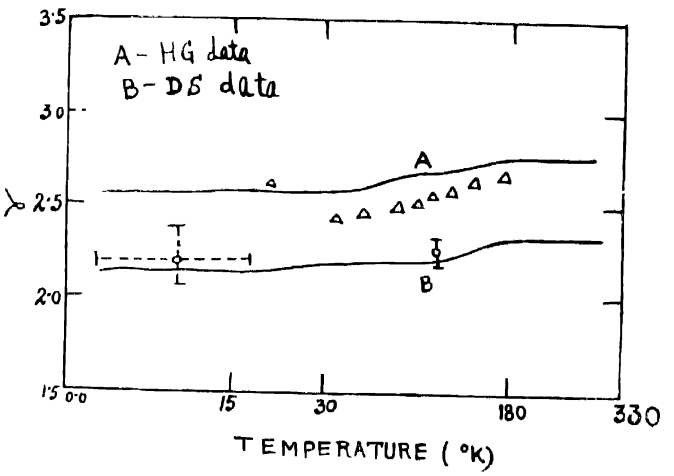


Fig. 3. The Grüneisen parameter of gold as a function of temperature. The continuous curves correspond to present calculation. Experimental observations are indicated by Δ Fraser and Hollis-Halltt, —O— (Carruccini and Gniewek).

Acknowledgments

It is pleasure to thank Professor Vachaaspati, Head of the Physics Department, University of Allahabad, for encouragement and for providing facilities

for the study. We are particularly indebted to Dr. Jyoti Prakash for many stimulating discussions. We thank H. L. Kharoo for help in the numerical work. One of us (L.P.P.) gratefully acknowledge financial assistance from the horities of Allahabad University.

References

Barron T. H. K. 1955 *Phil. Mag.* **46**, 720.

—— 1957 *Annals of Physics* **1**, 77.

Betts D. D., Bhatia A. B. & Wyman M. 1956 *Phys Rev* **104**, 37

Behari J. & Tripathi B. B. 1969 *Phys. Lett* **29A**, 313.

Blackman M. 1957 *Proc. Phys. Soc.* (*London*) **B7**, 827

—— 1958 *Phil. Mag.* **3**, 831.

—— 1959 *Proc. Phys. Soc.* (London) **B74** 17.

Carr R. H., McCammon R. D. & White G. K. 1964, *Proc Roy. Soc.* **A280**, 72.

Corruccini R. J. & Gniewek J. J. *Thermal expansion of Technical Solids at low temperature* (National Bureau of Standards) Washington, 1961.

Daniels W. B. and Smith C. S. 1958 *Phys. Rev* **111**, 713.

Fraser D. B. and Hollis-Hallet A. C. 1965 *Canad. J. Phys.* **43**, 193.

Gellmann M. & Bruckner K. A. 1957 *Phys. Rev.* **106**, **364**.

Grueisen E. 1926 *In Hab. Phys.* 10. Eds. Flugge, Springer-Verlag, Berlin, p.1.

Hiki Y. & Granato A. V. 1966 *Phys Rev.* **144**, **411**.

Pathak L. P. Prakash J. & Chandra S. 1975 *Letter Al Nuovo Cimento* **13**, 83

Pathak L. P., Singh V. P. Prakash J. & Hemkar M. P. 1976 *Ind. J. Phys.* (Accepted for publication)

Pearson W. B. 1958 *A Handbook of Lattice Spacing* and *Structures of Metals and Alloys* (New York Pergamon Press Inc.).

Prakash J. and Hemkar M. P. 1973 *J. Phys. Soc. Japan* **34**, 1583.

—— *J. Phys. F. Metal Phys.* **4**, 1015.

Prakash J., Pathak L. P. & Hemkar M. P. 1974 *J. Phys. F. Metal Phys.* **4**, 1107.

—— 1975 *Aust. J. Phys.* **28** 63.

Rubin T., Altman H. W. & Johnston H. L. 1961 *J. Phys. Chem* **65**, 65.

Sheared F. W. 1958 *Phil. Mag.* **3**, 1381.

Toya T. 1961 *J. Res. Inst. Catalysis*, Hokkaido Univ. **9**, 1778.

White G. K. 1963 *Proc VIII International Conference on Low Temperature Physics* (Buttor Worth London, p. 391

Ziman J. M. 1960 *Electrons and Phonons* (Oxford. Clarendon Press)